RELATION

OF THE

CHEMICAL CONSTITUTION OF BODIES TO TASTE.

By Prof. E. N. Horsford, of Harvard.

Prof. Horsford alluded to a paper upon Glycocoll published in 1846, in which he called attention, in a note, to the interesting relation sustained by that body in its chemical constitution, to other sweet bodies, and cited the following formulæ:

$$C_4 H_3 \overset{H}{\underset{N}{}} O_3 = \text{Glycocoll.}$$

$$C_4 H_3 \overset{H}{\underset{O}{}} O_3 + 3 = \text{Grape sugar.}$$

$$C_4 H_3 \overset{Pb}{\underset{O}{}} O_3 = \text{Sugar of lead.}$$

$$C_4 H_3 \begin{matrix} H \\ H\frac{2}{3} \end{matrix} O_{3\frac{1}{3}} = \tfrac{2}{3} \text{ Oxide of glycerile.}$$

To this enumeration of sweet bodies was appended the query, "Is this similar taste dependent upon a similar arrangement of their minutest particles?"

Prof. H. remarked that, early in 1848, he presented to the American Academy of Arts and Sciences, with a modification of the formula, an additional list of sweet bodies. Some of the formulæ were arbitrarily doubled from the received formulæ, and others fractionally reduced, for the sake, merely, of tracing this interesting relationship.

The modification of the formulæ, and the list as then presented, were as follows:

$C_4H_4O_4 \times 3$ = Grape sugar.

$C_4H_2 \begin{matrix} H \\ H \\ O \end{matrix} O_3$ = " "

$C_4H_2 \begin{matrix} H \\ H \\ N \end{matrix} O_3$ = Glycocoll.

$C_4H_2 \begin{matrix} Pb \\ H \\ O \end{matrix} O_3$ = Sugar of lead.

$C_4H_2 \begin{matrix} O \\ PbO_3 \cdot 3 \\ O \end{matrix}$ = Citrate of lead.

$C_4H_2 \begin{matrix} O \\ K \\ O \end{matrix} O_3$ = Acetate of potassa.

$C_4H_2 \begin{matrix} H \\ H \\ N \end{matrix} O_2, H, O,$ = Nitric ether.

$C_4H_2 \begin{matrix} H \\ H \\ H_{\frac{2}{3}}O_{\frac{1}{3}} \end{matrix} O_3 \times 1{\cdot}5$ = Oxide of Glycerile.

$C_4H_2 \begin{matrix} Cl \\ Cl_3 \\ Cl \end{matrix} \div 2$ = Chloroform.

$C_4H_2 \begin{matrix} Br \\ Br_3 \\ Br \end{matrix} \div 2$ = Bromoform.*

$C_4H_2 \begin{matrix} I \\ I_3 \\ I \end{matrix} \div 2$ = Iodoform.

$C_4H_2 \begin{matrix} I \\ Cl_3 \\ Cl \end{matrix} \div 2$ = Chloroiodoform.

$C_4H_2 \begin{matrix} Br \\ I_3 \\ I \end{matrix} \div 2$ = Bromoiodoform.

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* For the observation that this and the following four bodies may be included under this type, the author acknowledged his indebtedness to his assistant, Dr. Chas. H. Peirce.

$$C_4H_2\begin{matrix}H\\H\\H\end{matrix}\begin{matrix}H\\F_2\end{matrix} \div 2 = \text{Hydrofluate of methylene.}^*$$

$$C_4H_2\begin{matrix}S\\S\\S\end{matrix}S_3 \div 2 = \text{Sulphoform.}$$

$$C_4H_2\begin{matrix}H\\H\\H\end{matrix}\begin{matrix}H\\Cl_2\end{matrix} \div 2 = \text{Chloride of Methyle.}$$

$$\begin{matrix}C_2\\S_2\end{matrix}H_2\begin{matrix}O\\Ag\\O\end{matrix}O_3, H, O, = \text{Methylsulphite of silver.}$$

$$\begin{matrix}C_2\\S_2\end{matrix}H_2\begin{matrix}O\\Pb\\O\end{matrix}, H, O, = \text{Methylsulphite of lead.}$$

$$\begin{matrix}C_2\\S_2\end{matrix}\begin{matrix}H\\Ag\end{matrix}\begin{matrix}O\\Cl\\O\end{matrix}O_3, H, O = \text{Chloro-methylsulphite of silver.}$$

$$\begin{matrix}C_2\\S_2\end{matrix}\begin{matrix}H\\Pb\end{matrix}\begin{matrix}O\\Cl\\O\end{matrix}O_3, H, O = \quad " \quad " \quad \text{lead.}$$

$$S_4\,Ag_2\begin{matrix}O\\O\\O\end{matrix}O_3 \div 2 = \text{Hypo-sulphite of silver.}^\dagger$$

$$S_4\begin{matrix}Na\\Hg\end{matrix}\begin{matrix}O\\O\\O\end{matrix}O_3 = \text{Hypo-sulphite of mercury and soda}$$

To these Prof. Horsford remarked there might be added

$$C_4\,H_2\begin{matrix}H_2\\O\end{matrix}O_3 \cdot 3 + H_2 = \text{Mannite ; and}$$

$$C_4\,H_4\,S_4.$$

Several other compounds of sulphur with $C_4\,H_4$ do not taste sweet.

The following sweet bodies, one possessing a multiple and the other nearly a multiple of the number of atoms in Glycocoll, do not readily admit of being written in the above formula—

$$C_{10}\,H_{11}\,O_3 = 24 = \text{Valerianic acid.}$$

$$C_{16}\,H_{11}\,O_7 = 34 = \text{Orcine.}$$

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* This body has a pleasant etherial smell.

† The correspondence in constitution of this body with the next in succession gives additional interest to the formula.

In reply to the inquiry as to whether sweetness may be ascribed to a peculiarity of form, the following facts are of significance:

$C_4 H_4 S_4$ tastes sweet, and contains C, H and S.
$C_4 H_4 O_4$ " " C, H and O.
$S_4 \overset{O_2}{Ag_2} O_4$ " " neither C nor H.

The taste is, therefore, not dependent upon any one of the elements present, since each may be replaced entirely by another without destroying the taste.

In the communication submitted to the American Academy, attention was directed to the common formula, in which, according to Davy and to most modern chemists, all the acids containing hydrogen may be written, and also the oxygen acids which ordinarily exist in combination with an atom of water, as sulphuric and nitric acids; to wit, $H + x$; in which x represents all that part of the acid not replaced by metal in neutralization. A few examples follow:

$H + Cl$	= Hydrochloric acid.	$H + NO_6$	= Nitric acid.
$H + I$	= Hydriodic "	$H + C_2HO_4$	= Formic "
$H + Br$	= Hydrobromic "	$H + C_2O_4$	= Oxalic "
$H + F$	= Hydrofluoric "	$H + C_4H_3O_4$	= Acetic "
$H + Cy$	= Hydrocyanic "	$H + C_6H_5O_4$	= Metacetonic "
$H + SO_3$	= Sulphurous "	$H + C_8H_7O_4$	= Butyric. "
$H + SO_4$	= Sulphuric "	$H + C_{10}H_{11}O_4$	= Valerianic " &c.

The inquiry naturally arises, have sour bodies a common *form?* to which, and not to the nature of the constituent particles, the property of sourness is to be attributed. They (the acids) are composed of one larger atom, or group of atoms united to the least atom, hydrogen, easily replaceable by a metal, and bound to the group by an affinity apparently much feebler than that of any of the remaining elements.

An allusion was made, in the communication to the Academy, to the class of resins—some of the soluble members of which possessing a bitter taste—might, according to a research of Heldt upon Santonine, be referred to a single fundamental type. He refers the resins, for their origin, to the oxidation of the essential oils, and though the conception has been entertained by other chemists, it has first met with a full exposition in this paper. The hydrogen of essential oils oxidates,

as a general thing, much more readily than the carbon. The following formulæ present Heldt's view of the production of resins. All are derived, he conceives, from $C_{10}H_8$.

$$[C_{10}H_8]^n - Hx + Ox = R.$$
$$[C_{10}H_8]^n - Hx + Ox + (HO)y = R.$$
$$[C_{10}H_8]^n - Hx + Ox + Oy = R.$$
$$[C_{10}H_8]^n - Hx + Ox + Oy + [HO]z = R.$$
$$[C_{10}H_8]^n + [HO]x = R.$$

These formulæ present in the original essential oils, groups of atoms, in which a part of the hydrogen occupies a more exposed situation, if one may employ the illustration, than other parts of the molecule, and oxidates more readily. In this respect there is approximation to a common form, in view of which the inquiry was suggested, *may the bitterness be ascribed to this form?* This, however, does not furnish an explanation of the remarkable bitterness of the organic bases.

Guided by the above suggestion, Prof. H. remarked, let the conception be entertained that the alkaloids have been derived from the greater or less oxidation of bodies having the general constitution of the essential oils, and the replacement of three atoms of water with one atom of ammonia for every atom of nitrogen contained in the organic base. The corresponding replacement of ammonia with three atoms of water is not of unfrequent occurrence in organic chemistry.

Upon the speculation that this has been the derivation of the alkaloids, it will be easy to convert them into the essential oils from which they were derived. If we halve the formula of the oil, the first of Heldt's formulæ gives

$$(C_5H_4)^n - Hx + Ox = R.$$

A certain number of atoms of hydrogen deducted from, and an equal number of atoms of oxygen added to, n times C_5H_4 constitute the resin. If, in adding nitrogen, we deduct for each atom of nitrogen three atoms of oxygen, or, which is the same thing, for each atom of ammonia (NH_3) added, deduct three atoms of water, we have an organic body containing C, H, N and O, a body corresponding in constitution with an alkaloid.

By reversing this process, we may convert the alkaloid into its corresponding essential oil.

Take for example Papaverin, one of the alkaloids of opium, analyzed by Merck. $C_{40}H_{21}NO_8$.*

Three atoms of oxygen for the atom of nitrogen, united to the eight atoms of oxygen, making eleven in all, correspond with eleven atoms of hydrogen, which, added to the twenty-one present, make thirty-two.

$$C_{40}H_{21}NO_8 - N - O_8 + H_8 + O_3 = C_{40}H_{29} + O_3,$$

which correspond with

$$C_{40}H_{32} = (C_5H_4)^8.$$

There is doubt still resting upon the constitution of most of the alkaloids. Of those considered as best established, the following examples will be sufficient for a practical illustration of the above speculation.

$$\text{Thebain} = C_{25}H_{14}NO_3 = C_{25}H_{20} = (C_5H_4)^5.$$
$$\text{Furfurin} = C_{30}H_{12}N_2O_6 = C_{30}H_{24} = (C_5H_4)^6.$$
$$\text{Codein} = C_{35}H_{20}NO_5 = C_{35}H_{28} = (C_5H_4)^7.$$

The formula $(C_5H_4)^n - H_x + O_x + O_y = R$, is suited to the derivation of Bebeerin.

$$C_{35}H_{20}NO_6 = C_{35}H_{29} = (C_5H_4)^7 + H.$$

Harmalin requires the addition of C_2H_2 to the second of Heldt's formulæ $(C_5H_4) - H + O_y = R$.

$$C_{27}H_{14}N_2O_2 = C_{27}H_{22} = (C_5H_4)^6 + C_2H_2.$$

Chinin and Cinchonin require the subtraction of C_2.

$$\text{Chinin} = C_{38}H_{22}N_2O_4\dagger = C_{38}H_{32} = (C_5H_4)^8 - C_2.$$
$$\text{Cinchonin} = C_{38}H_{22}N_2O_4\ddagger = C_{38}H_{32} = (C_5H_4)^8 - C_2.$$

Strichnin requires the deduction of an atom of carbonic acid, or its equivalent CH_2, and the same formula of resin as that of Bebeerin.

$$C_{44}H_{24}N_2O_4 = C_{44}H_{34} = (C_5H_4)^9 - CH_2.$$

Cotarnin requires the addition of an atom of carbonic acid.

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* Liebig's Ann., LXVI., 125; Pharm. Contr., 1848, 930.

† Ann. Ch. Phys. [3] XIX., 363; Ann. d. Ch. u. Phar. LXII., 95.

‡ Ann. Ch. Phys. [3] XIX., 365.

$$C_{26}H_{13}NO_6{}^{*} = C_{26}H_{22} = (C_5H_4)^5 + CH_2.$$

The following require slight modifications.

$$\text{Morphin} = C_{34}H_{19}NO_6{}^{\dagger} = C_{34}H_{28} = (C_5H_4)^7 - C.$$
$$\text{Piperin} = C_{34}H_{19}NO_6{}^{\ddagger} = C_{34}H_{28} = (C_5H_4)^7 - C.$$
$$\text{Veratrin} = C_{34}H_{22}NO_6 = C_{34}H_{31} = (C_5H_4)^7 - C + H_3.$$

It will readily be seen that in this series the differences between the essential oil and its derivative are such as would disappear with the addition or subtraction of an atom of carbonic acid, or water in some cases, and a little more or less oxidation in others.

In those bases where the quantity of nitrogen is much larger, the third formula of Heldt would still give us the corresponding resins.

$$(C_5H_4)_n - Hx + Ox + Oy = R.$$

Take for example Caffein.

$$C_{14}H_8N_4O_4.$$

The nearest essential oil of the constitution $(C_5H_4)^n$ is $C_{15}H_{12}$.

$$C_{15}H_{12} - H_4 + O_4 + O_{14} + 4(H_3N) - 12\,HO = C_{15}H_8N_4O_6.$$

If we deduct from this formula an atom of carbonic acid, we have

$$C_{15}H_8N_4O_6 - CO_2 = C_{14}H_8N_4O_4.$$

Theobromin differs, as has been remarked,§ from Caffein only by C_2H_2.

$$C_{14}H_8N_4O_4 + C_2H_2 = C_{16}H_{10}N_4O_4.$$

The construction from the class of oils, above referred to, of the formulæ of those alkaloids in which the quantity of hydrogen is much greater, is more difficult.

The foregoing relationships have an interest taken in connection with the inquiry to which attention has been directed, to wit, *May there be a common form among bodies having a common taste?*

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* Ann. Ch. Phys. [3] XIX., 370.

† Ann. Ch. Phys. [3] XIX., 361; Ann. d. Ch. u. Phar. LXIII., 98.

‡ Ann. Ch. Phys. [3] XIX., 363.

§ Ann. d. Ch. u. Pharm., LXI., 338? Pharm. Cont. Blatt., 1847, 424.